

科目：有機化學 適用：應化所

編號：441

考生注意：

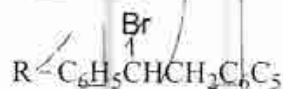
1. 依次序作答，只要標明題號，不必抄題。
2. 答案必須寫在答案卷上，否則不予計分。
3. 限用藍、黑色筆作答；試題須隨卷繳回。

本 試 題

共 3 頁

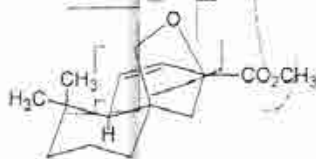
第 1 頁

1. Write formulas for all possible dibromo products from the monobromination of the following compound. Which of the dibromo products would be optically active? (10%)

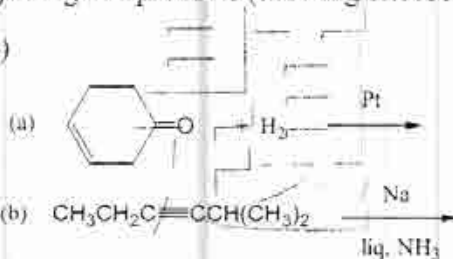


2. A chemist treated $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$ with magnesium in anhydrous ether and then added acetone (propanone). After hydrolysis, instead of a single alkenyl alcohol as a product, the chemist obtained two alcohols. What are the structures of the two alcohols? Explain your answer. (10%)

3. During an investigation of naturally occurring antitumor agents, the following compound was subjected to OsO_4 oxidation, followed by treatment with NaHSO_3 . A single stereoisomeric product was obtained in 93% yield. What was this product? (10%)



4. Predict the major organic products (showing stereochemistry): (10%; 5% each)



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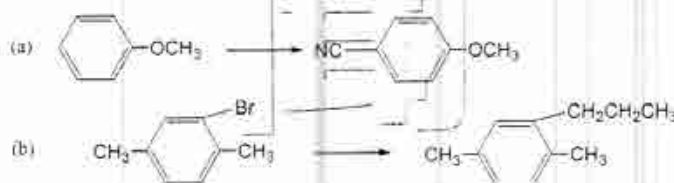
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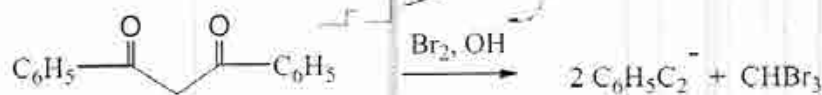
第 2 頁

5. *Muscalure*, the sex attractant of the common housefly (*Musca domestica*), is a hydrocarbon with the formula $C_{23}H_{46}$. Catalytic hydrogenation of this compound yields $C_{23}H_{48}$, while oxidation with a hot, alkaline solution of $KMnO_4$ followed by acidification yields $CH_3(CH_2)_{12}CO_2H$ and $CH_3(CH_2)_7CO_2H$. Addition of bromine to the hydrocarbon yields one pair of enantiomeric dibromides ($C_{23}H_{46}Br_2$). What is the structure of the housefly sex attractant? (10%)

6. How would you make the following conversions? (10%; 5% each)



7. When 1,3-diphenyl-1,3-propanedione reacts with alkaline Br_2 , it gives bromoform and benzoate ion instead of 2,2-dibromo-1,3-diphenyl-1,3-propanedione, which might have been anticipated at first glance. Write chemical equations to show how this reaction could occur. (10%)



8. The reaction of 2-methyl-1,3-butadiene (isoprene), used in the manufacture of rubber and other polymers, with HCl at 25° yields compounds A and B in a ratio of 75:25. Write mechanisms for the formation of these compounds. (10%)

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9. *cis*-Jasmone, a principal odorous component of jasmine oil, can be synthesized by heating the 11-carbon compound *cis*-8-undecen-2,5-dione with basic alumina (Al_2O_3) in benzene. The infrared spectrum of *cis*-jasmone shows principal peaks at 1645 cm^{-1} ($6.08\text{ }\mu\text{m}$) and 1700 cm^{-1} ($5.88\text{ }\mu\text{m}$). The molecular weight was determined by mass spectrometry to be 164. The ^1H NMR spectrum shows the following absorption. What is the structure of *cis*-jasmone? (10%)

δ	splitting	relative area
5.25	multiplet	2
2.85	doublet	2
1.9-2.7	multiplet	6
2.05	singlet	3
0.95	triplet	3

10. A chemist attempted to carry out a Hofmann rearrangement of butanamide with bromine and potassium hydroxide in methanol, rather than in water. Instead of propylamine, the chemist obtained a carbamate, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NHCO}_2\text{CH}_3$. Explain how this product was formed. (10%)